

CO₂ capture using lime as sorbent in a carbonation/calcination cycle

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Abstract

In order to mitigate the CO₂ emissions from coal power generation systems efforts are being devoted worldwide to improve the existing capture technologies and to develop lower cost processes to separate CO₂.

The lime carbonation/calcination cycle is based on separation of CO₂ with the use of lime as an effective CO₂ sorbent. Previous work has been carried out in an entrained flow calciner studying the flash calcination process for the preparation of lime [1].

The current work is focused on advanced dry CO₂ capture system applicable for both PF and CFB boilers, using lime as sorbent. A twin fluidized bed carbonator/calciner system is used in order to study the impact of flue gas contaminants and sorbent post-treatment for sulphur separation, to evaluate the optimized calcination process (with O₂-firing, steam addition, varying CO₂ levels, etc.).

Topic: Capture and Separation /Advanced Concepts

Introduction

Fossil fuel plants will continue to be required in developed and developing countries in the coming decades as fossil fuel is still the most important energy source, 80% of global energy use relying on it. In order to manage the conflict between increasing demand for electric power and increasing concerns over climate change, strategies for supplying low-carbon power are being pursued. The effects on climate change of the increasing CO₂ emissions in the atmosphere represent the driving force for the development of advanced energy cycles incorporating CO₂ management options. The great interest in the technical and economic feasibility of capturing CO₂ from large coal-based power plants increased the efforts devoted worldwide to develop new concepts for greater CO₂ reductions in the future.

Post combustion capture is a well-established technology which can be delivered commercially but needs scaled-up engineering and optimization to be able to be applied to large scale power plants. Therefore, the challenge for post-combustion capture systems is to develop new designs for commercial-scale applications in large industrial facilities.

Post-combustion capture system (Figure 1) includes the power plant island and a large scale new device to separate the CO₂ from flue gas after combustion at low pressure (atmospheric) and low CO₂ content (3-20%). The capture unit is an end-of-pipe unit, even if the power and capture plant are partly integrated as steam is extracted from the power plant for CO₂ regeneration.

Several methods can in principle be considered for the large-scale separation: scrubbing of gases with a liquid solvent, solid sorbents, separation with membranes, and cryogenics.

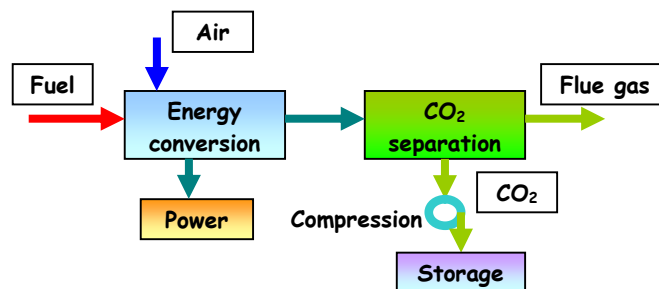


Figure 1. Post combustion scheme

Chemical absorption of CO₂ by means of MEA is commercially applied, but not on such a large scale as required for CO₂ capture at power generation plants. The CO₂ is stripped from the amine solution, dried, compressed and transported to the storage site. Amine scrubbing capture is a high energy consuming process as it requires lots of heat for solvent regeneration and, because it operates at atmospheric pressure, it also requires a lot of energy to compress the CO₂ for transportation.

Post-combustion CO₂ removal processes have to deal with low gas pressure, low partial pressure of CO₂ and trace elements like SO₂ and NO_x that need to be removed prior to entering the absorber, as their removal to low concentrations is essential, since these components form heat stable, corrosive salts that cause operational problems and solvent losses. Flue gas conditioning steps are also costly and energy intensive. Parasitic losses for thermal power plants that use amine scrubbing ranges between 10 and 30% of the total power generated if CO₂ capture were not included [2].

As the cost of the separation of CO₂ from flue gases introduces the largest economic penalty, a range of emerging approaches to separate CO₂ with more cost-effective processes is justified. An intense research activity exists all over the world to develop lower cost processes to separate CO₂.

The proposed lime carbonation/calcination cycle is based on separation of CO₂ from combustion gases with the use of lime as an effective CO₂ sorbent to form CaCO₃. The reverse calcination reaction produces a gas stream rich in CO₂ and supply sorbent (CaO) for subsequent cycles of carbonation. The concept could in principle be applied as a retrofit of existing plants or as new power plant.

Carbonation/calcination cycle

The principle of separation follows the scheme of Figure 2 with the separation of CO₂ carried out at high temperature using CaO as regenerable sorbent.

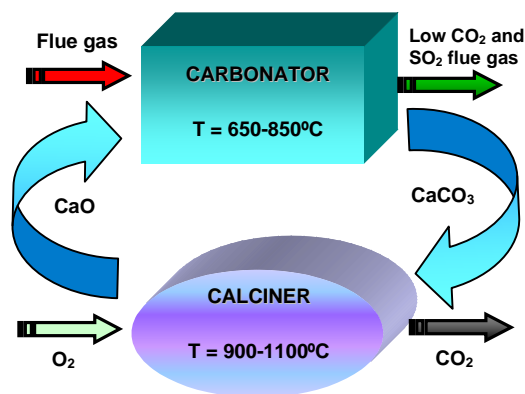


Figure 2. Lime Carbonation/Calcination Cycle

This process was first described by Shimizu et al. [3] and overall system performance have been simulated, although the sorbent decay data and experimental validation of the key units (carbonator and calciner) were never included.

CaO particles react with CO₂ from combustion flue gases, at atmospheric pressure and temperature around 650°C, to produce CaCO₃. The carbonation reaction would take place in a reactor similar to a circulating fluidized bed combustor. The particles of CaCO₃ are then separated from the flue gas and sent to a different vessel for regeneration (calcination to produce

pure CO₂ suitable for storage and CaO). Then, the newly formed CaO is resubmitted again to the capture step. The main option considered at present for the calcination step is oxy-firing coal in a fluidized bed calciner at temperature over 900°C, with the calcined solids cycled continuously to the carbonation step, a CO₂ chemical loop being established between the carbonation and calcination reactors.

The potential advantage of this system is the very low efficiency penalty expected (<6%) compared with other capture technologies as the heat required for calcination is released during carbonation and can be utilised efficiently at high temperature in the steam cycle of the boiler. High concentrated CO₂ stream can be generated when using oxygen blown calcination. The proposed technology can be compared to wet scrubbers using amines for CO₂ absorption as these scrubbers need also a regenerator operating at higher temperatures than the absorber, but at a considerably lower temperature level compared to the lime loop. Since limestone is a cheap material with good geographical distribution, it allows the use of local limestone resources from power plants for CO₂ capture with minimal limestone-related infrastructure investment. The purge lime from the cycle will be used as a raw material for the production of cement clinker. Efficiency losses of this process are those associated to compression of CO₂ and calcination of the relatively large make up flow of limestone required to keep the activity of the sorbent. The large flow of CaO required to capture CO₂ ensures that SO₂ is also removed from the flue gases

The main concerns associated with this system are sorbent reactivity, sorbent durability and the effects of SO_x in the flue gas. The decay in carbonation conversion with number of cycles is shown Figure 3 [1].

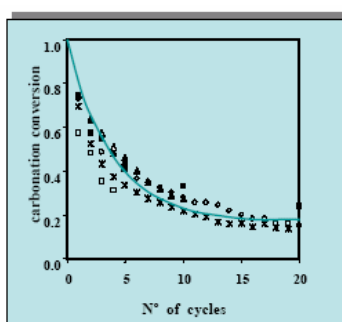


Figure 3. Decay in carbonation conversion with number of cycles

Previous work

Initial investigations were carried out in an entrained flow calciner in order to study the flash calcination process for the preparation of lime. Results obtained showed the important role played by the particle size in calcination process, a lime conversion of 99% at 550°C leading to predicted levels of CO₂ reduction of 85 % [1].

Current work

The current work is focused on advanced dry CO₂ capture system, using lime as sorbent, applicable for both PF and CFB boilers. A twin fluidized bed carbonator/calciner system is used in order to study the impact of flue gas contaminants and sorbent post-treatment for sulphur separation, to evaluate the optimized calcination process (with O₂-firing, steam addition, different CO₂ concentrations, etc.), to study the coupled carbonation/ calcination process in order to determine the best suitable parameters (fluidization velocity, particle size, temperatures and residences times).

Rig design

The design of the rig offering continuous carbonation - calcination has been finalised and the construction is almost ready. The rig will allow the adjustment of the residence time of solids in the reactors, by a mechanism able to split the solids coming from the cyclone into two solid streams under control. This represents a very important step in the optimisation of the process since it allows an appropriate circulation rate between the carbonator and the calciner according with the needs of the process, avoiding high energy consumption associated with high circulation rates which would be otherwise needed in order to heat up the extra solids to calcination temperature.

The scheme of the facility is given by Figure 4.

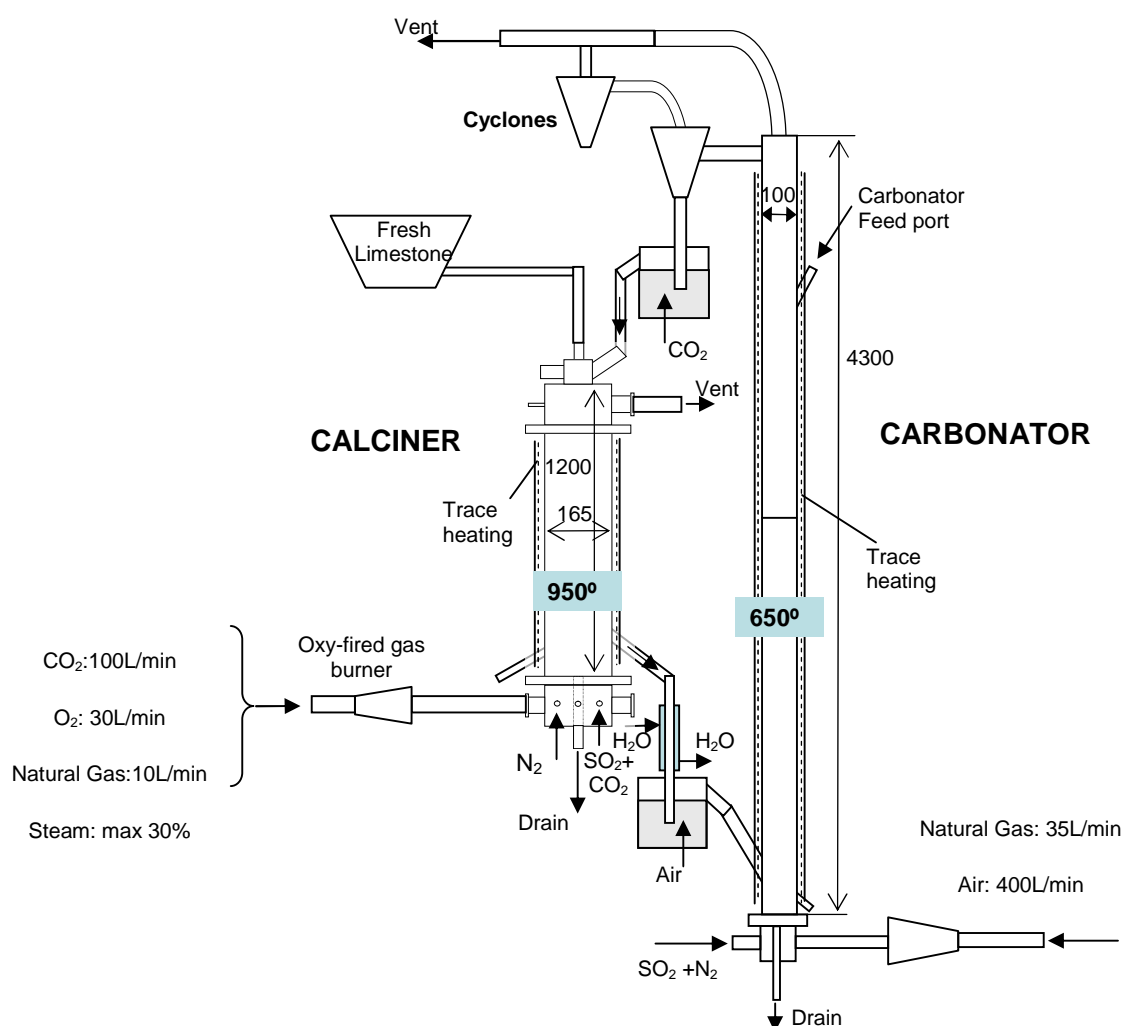


Figure 4. Test rig

The rig is based around two units - a bubbling fluidised bed, the calciner, and a circulated fluidised bed, the carbonator. The vessels can be operated either separately or coupled. The rig includes facilities for full sampling and routine flue gas measurements, data logging of operational parameters, having automated operation on natural gas.

Operating Conditions

The carbonator is a circulating fluidized bed reactor with a length of 4.5 m and a diameter of 0.10 m, fluidized with flue gas produced in a natural gas burner of 25 kW, the typical gas

velocities being in the range of 3-4 m/s. An electrical heating system maintains an operating temperature of 650-850°C. The flue gas fed in the carbonator has a typical CO₂ concentration of 8%. In order to simulate a coal flue gas, a stream of SO₂ (coming from commercial gas bottles) is added. The system used is able to vary the SO₂ concentration into the reactor.

The calciner, a bubbling fluidized bed reactor, is used to carry out subsequent testing on the absorption capacity of sorbent materials, the effect of calcination conditions on sorbent capacity and the effect of sulphur separation from used sorbent.

To achieve a reasonable level of conversion, the residence time has to be in the range of a few seconds, and this, combined with the minimum gas flow in the line needed to avoid the effect of gas dispersion, gave the required length for the reactor. The reaction chamber has a length of 1.2 m and diameter of 0.16 m. Solids (limestone and fresh limestone) are fed from the top of the vessel using a hopper with a screw feeder.

The calciner is oxy-fired and the flue gas stream will be doped using SO₂ and steam. With this system the CO₂ concentration can be increased to a higher value of about 95%. The steam concentration can be varied until a value of 20% is reached. The reactor chamber temperature profile is controlled by an electrical trace heating system, giving the possibility to adjust the temperature for each type of test (900-1100°C).

Experimental work

Three types of experiments will be performed in this rig: single carbonation, single calcinations and cycles of carbonation and calcination tests. Calcination tests will be done in a continuous mode and the carbonation trials and carbonation/calcination cycles will be carried out in batch mode.

Calcination tests will be focussed on the process performance at high CO₂ partial pressures and will also investigate the SO₂ and steam effect on the sorbent.

Carbonation will be done to study the absorption capacity of fresh sorbents and the effect of different SO₂ concentrations. The sorbents will be loaded into the bed and the flow gases will be passed through the bed until sorbent saturation is reached.

The experiments will investigate the feasibility of the **coupled carbonation/calcination** processes in the continuous mode under atmospheric pressure in order to validate the best suitable parameters (fluidization velocity, particle size, temperatures and residences times). A series of tests with different SO₂ concentrations in the calciner and carbonator will be carried out, the results being essential in understanding the SO₂ effect in CO₂ capture process. Additionally tests with added steam will investigate the effect of the steam in the absorption capacity of the regenerated sorbent.

In those experiments a total solids inventory of 15-25 kg will be used (about 10 kg in the calciner and 5-10 kg in the carbonator), the gas flow rate for the calciner will be about 100-150 L/min, and 400-500 L/min for the carbonator.

Table 1 summarizes the experimental planning for the coupled tests for each sorbent that has to be tested.

Table 1. Test matrix for coupled carbonation/ calcination experiments

Test	SO ₂ (ppm)		Steam (%) ²		CO ₂ (%)	
	Calcination	Carbonation	Calcination	Carbonation	Calcination	Carbonation ¹
1	0	0	0	0	100	15
2	500	0	0	0	100	15
3	1000	0	0	0	100	15
4	1500	0	0	0	100	15
5	0	500	0	0	100	15
6	0	1000	0	0	100	15

Test	SO ₂ (ppm)		Steam (%) ²		CO ₂ (%)	
	Calcination	Carbonation	Calcination	Carbonation	Calcination	Carbonation ¹
7	0	1500	0	0	100	15
8	500	500	0	0	100	15
9	500	0	5	0	95	15
10	500	0	10	0	90	15
11	500	0	15	0	85	15
12	500	500	Opt. ³	0	Opt. ³	15

¹CO₂ in carbonator will depend on combustion conditions and if added CO₂ is used

²Steam refers to the added steam. Not considering the steam produced during the combustion

³Opt. means the optimal steam concentration obtained in tests with SO₂ and steam in the calciner

Proposed post-combustion fluidized bed system for CO₂ capture

Figure 5 presents the assessment of mass and heat flow balances for the proposed post combustion fluidized bed system for CO₂ capture using lime carbonation/calcination cycle. A typical coal with a lower heating value of 25 MJ/Kg has been selected as fuel.

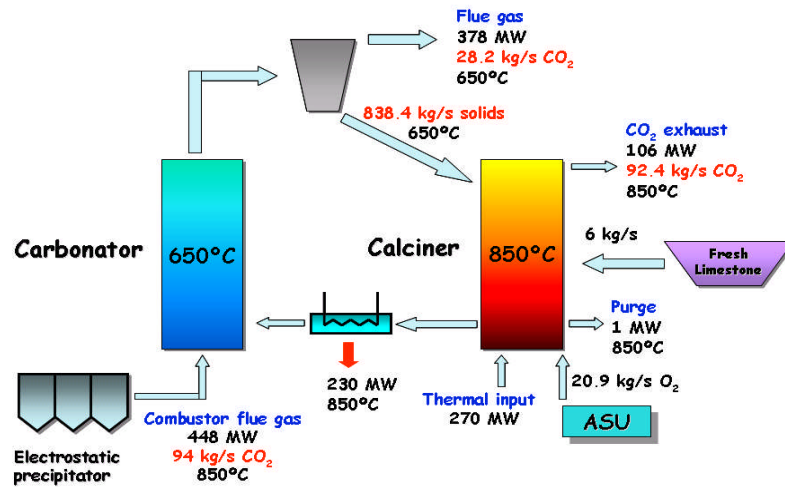


Figure 5. Post combustion fluidized bed system for CO₂ capture

The sulphur content and its effect on CO₂ capture was neglected in order to simplify the study. A mass flow of 94 kg/s of CO₂ exit from the power island. The heat balance takes into account the heat generated in the calcination process and particle and gas flows through the calciner. The lime flow in the calciner was calculated assuming a CO₂ retention efficiency of 0.3. At the exit of the calciner, particles were removed from the flue gases. The calciner unit used to regenerate the limestone is heated with a mixture of natural gas and oxygen. In the calciner heat balance, a working temperature of 850 °C was assumed. Products formed in the calciner will pass through a heat exchanger unit.

The parametric experiments using a calcium-based sorbent will be carried out, as mentioned above, in order to identify optimal process parameters for absorption and regeneration and the parameters affecting the system performance.

Results obtained from this study are essential in order to understand the impact of SO_x on the sorbent and avoid high solid purge rates.

References

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